Catalytic Analysis. XIX : Rapid Microdetermination of Copper in Various Metals

Catalytic Analysis. XIX
Rapid Microdetermination of Copper in Various Metals*

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Synopsis

Copper has a catalytic action on the reduction of ferric ion in an acidic solution with sodium thiosulfate. Effects of various metals and concentrations of acids on this reaction were studied. By measuring the time required until the dark violet of ferric thiosulfate complex in the presence of potassium thiocyanate was decolorized under a constant condition, the determination of microamount of copper, as small as 0.001～0.1 per cent, in various metals was carried out.

I. Introduction

Applying the well-known catalytic action of copper on the reduction of ferric ion in an acidic solution with sodium thiosulfate, the microdetermination of copper was reported(1) and copper in iron and steel was also determined(2) rapidly. In the present report, the determination of traces of copper in various metals was investigated with the same method.

II. Experimental results

1. Reagents

Ferric sulfate solution was prepared by dissolving ferric sulfate containing 1 g of iron first in 80 ml of sulfuric acid (1 : 1) and then diluting it to 1 liter. One milliliter of this solution thus contained 1 mg of iron. The mixed solution of sodium thiosulfate and potassium thiocyanate was prepared by dissolving 62.5 g of sodium thiosulfate and 25 g of potassium thiocyanate first in redistilled water and the diluting it to 1 liter. Redistilled water was used throughout the experiments.

2. Procedure

Pulfrich's photometer and other colorimeters were used in the previous experiments, but in the present case only the beaker of usual type was used without any special equipment.

In a 300 ml beaker, the known amount of copper or the sample solution was mixed with 50 ml of the ferric sulfate solution, and diluted to 150 ml with water and then it was controlled at 20°C. When 10 ml of the mixed solution of sodium thiosulfate and potassium thiocyanate was added as rapidly as possible and the

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* The 661st report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, **71** (1950), 353.

(1) H. Gotô and E. Sudô, the Journal of the Chemical Society of Japan, **64** (1943), 509, Sci. Rep. RITU, **A 1** (1949), 39.

(2) H. Gotô and T. Akizuki, the Journal of Japan Institute of Metals, **8** (1944), 664.

solution was vigorously shaken, the time measurement was begun. The time required for decolorizing the dark violet solution in the beaker placed on a white plate was measured, and the relation between the amount of copper and the time measured was obtained, fom which the amount of copper in the sample was determined.

3. Effect of the concentration of acid

It was already reported that this reaction took place in weak acidic solution. If the sample is dissolved in a definite volume of the acid, copper can immediately be determined; this will be a very simple and rapid method of determination of copper in various metals. Therefore, influences of various acids were studied in various concentrations in the presence of 10 γ of copper, other conditions being kept constant. Results obtained are shown in Table 1, from which it will be seen that, in sulfuric acid, the reaction velocity decreases in the case of lower concentration, while it increases in the case of higher concentration and that, in other acids, it is the opposite of the above. It was found, however, that the microamount of copper in various metals could be determined in a definite concentration of acid.

Table 1.

Acid used (ml)	Time measured (mean of twice) (sec)			
	HCl (1 : 1)	HNO_3 (1 : 1)	H_2SO_4 (1 : 1)	Aqua regia : water (1 : 1)
0	92.5	93.0	93.0	92.0
0.5	89.5	93.5	93.5	88.0
1.0	86.5	89.5	97.0	85.5
2.0	78.0	84.0	102.0	77.5
4.0	76.0	77.5	117.0	76.0
6.0	72.5	75.5	121.5	73.5
8.0	84.5	73.5	121.5	79.5
10.0	85.0	77.0	118.0	80.0
15.0	88.5	80.0	113.5	84.5
20.0	95.0	82.5	104.0	89.5
25.0	97.0	84.5	99.0	92.5
30.0	98.0	87.5	90.5	95.0

4. Effects of various metals

Next experiments on the influences of various metals in the presence of 10 γ of copper were made, other conditions being kept constant.

Lead used was lead nitrate together with 10 ml of nitric acid (1 : 1) and tin used was stannous chloride together with 10 ml of aqua regia. Aluminium used was a aluminium nitrate together with 10 ml of aqua regia and zinc used was a zinc nitrate together with 6 ml of nitric acid (1 : 1). As shown in Table 2, lead, tin and zinc did not affect the reaction velocity on varying the metal contents up to about 10 per cent, and aluminium did not perfectly influence this reaction on varying the amount of aluminium. The

Table 2.

Metals taken (g)	Time measured (mean of twice) (sec)			
	Pb	Sn	Al	Zn
0	77.5	90.5	91.0	75.0
0.3	111.5	102.0	91.0	84.0
0.4	103.0	111.5	90.5	95.5
0.5	99.5	115.5	91.0	97.0
0.6	97.5	116.0	90.5	100.0
0.7	89.0	124.0	91.5	110.0

Table 3.

Metals taken (g)	Time measured (mean of twice) (sec)			
	Mn	Ni	Co	Mg
0	77.0	76.5	78.0	80.5
0.3	90.5	89.5	121.0	92.5
0.4	98.0	96.0	128.0	103.5
0.5	100.0	101.0	130.5	109.0
0.6	99.5	106.5	131.0	112.5
0.7	108.0	114.5	139.5	122.5

linear function calibrated by a sample would be applied to the determination of microamount of copper in various metals, if the sample were weighed within the deviation of 10 per cent. Manganese, cobalt and nickel were used in their sulfates, respectively, together with 10 ml of nitric acid (1 : 1) and magnesium used was also a sulfate together with 6 ml of nitric acid (1 : 1). Copper was contained as impurities in nickel and cobalt salts, so it was removed by hydrogen sulfide treatment. As shown in Table 3, the reaction velocity was not affected on varying the metal contents up to 10 or 20 per cent. On the determination of copper in nickel or in cobalt, the sample solution was colorized and the observation of the end point of this reaction was somewhat difficult. If the sample solution were compared with the solution containing the same amount of metals and the same volume as the sample, it would be determined more easily. Cadmium used was its sulfate together with 3 ml of nitric acid (1 : 1) and mercuric chloride was used with 1 ml of aqua regia and bismuth used was its subnitrate together with 20 ml of nitric acid (1 : 1) and chromium used was chromic sulfate together with 5 ml of hydrochloric acid (1 : 1). Copper was contained in chromium salt as impurity. Therefore, it was removed by hydrogen sulfide. When the chromium contents were above 0.05 g, even if the sample solutions were compared with the solution containing the same amount of chromium as the sample solutions, the end point would not be found by the coloration of chromium salt. When 0.5g of bismuth or mercury was added, it took over a few hours until the dark violet was decolorized. As shown in Table 3, however, the reaction velocity was not so much affected on varying the metal contents up to 10~20 per cent.

Table 4.

Metals taken (g)	Time measured (mean of twice) (sec)			
	Cd	Hg	Bi	Cr
0	81.0	77.5	83.0	74.0
0.03	—	81.5	103.0	86.5
0.04	135.5	96.0	117.5	95.5
0.05	141.5	100.5	132.0	99.0
0.06	147.0	104.5	141.0	102.5
0.07	167.0	117.5	153.5	110.5

III. Determination of microamounts of copper in various metals

Determinations of microamounts of copper in various metals were made under the condition found by the preliminary experiments described above. The relation between the amount of copper and the time required in various concentrations of copper under the same condition was examined.

1. Lead, tin and nickel metals

Lead of 0.5 g was used together with 10 ml of nitric acid (1 : 1) and 0.5 g of tin was used together with 10 ml of aqua regia and 0.5 g of nickel was used together with 10 ml of nitric acid (1 : 1) and 0.05 g of it with 5 ml of nitric acid. The time was then measured by varying the copper content from 5 to 50 γ. When reciprocals of the time measured were plotted for the amount of copper, a linear relation was found as illustrated in Fig. 1.

2. Bismuth, magnesium and zinc metals

0.05 g of bismuth was used with 20 ml of nitric acid (1 : 1) and 0.5 g of magnesium

was added together with 15 ml of nitric acid (1 : 1) and 0.5 g of zinc was added together with 6 ml of nitric acid (1 : 1) and then the time was measured, using various amounts of copper. When reciprocals of the time measured were plotted for the amount of copper, a linear relation was obtained as illustrated in Fig. 2.

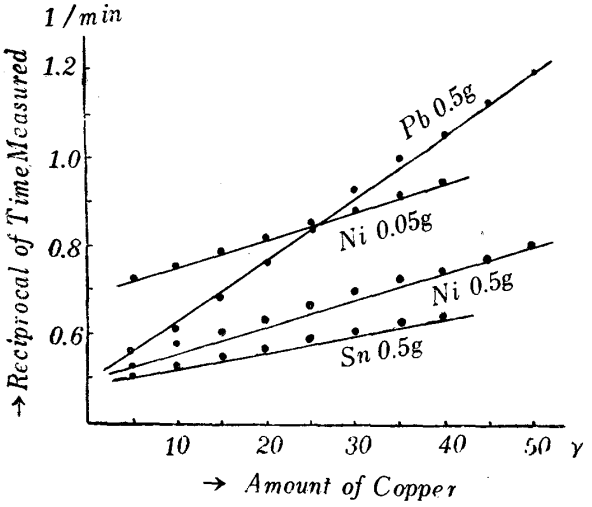

Fig. 1.

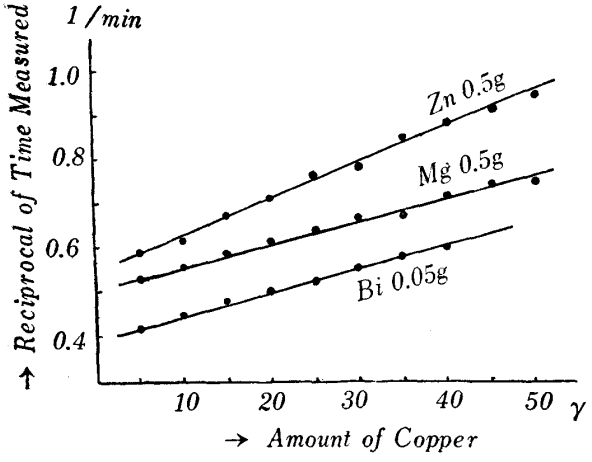

Fig. 2.

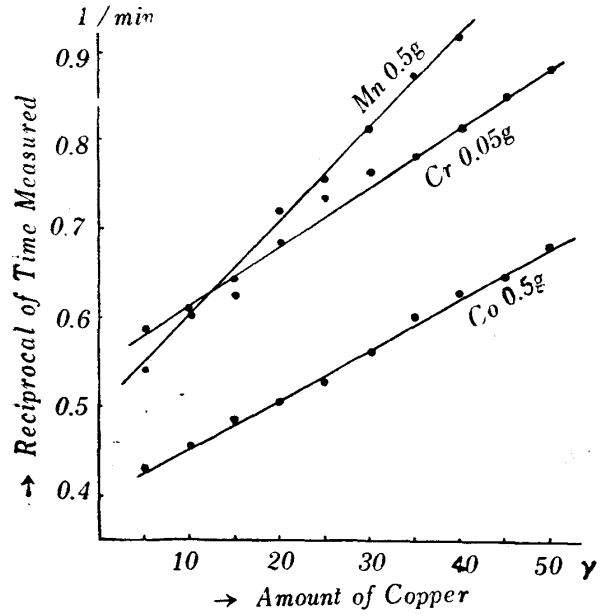

Fig. 3.

3. Manganese, cobalt and chromium metals

0.5 g of manganese and cobalt were used together with 10 ml of nitric acid (1 : 1) and 0.05 g of chromium was used with 5 ml of hydrochloric acid (1 : 1). The time measurements were made with various amounts of copper and the relations between the reciprocals of the time and the amount of copper are illustrated in Fig. 3.

4. Aluminium, mercury and cadmium metals

0.5 g of aluminium was used together with 10 ml of aqua regia and 0.05 g of mercury was used together with 1 ml of aqua regia and 0.05 g of cadmium was used together with 3 ml of nitric acid (1 : 1). The time required for decolorizing the solution was measured by varying the copper content. As shown in Fig. 4, the relations between the reciprocals of the time and the amounts of copper were linear. It was found that aluminium did not influence this reaction as described above and that applying only this linear relation, the determination of copper in aluminium metal was possible by the measurement of the time under the same condition. Microanalysis of copper in some metals was carried out by the above-described method, the results of

which are listed in Table 5.

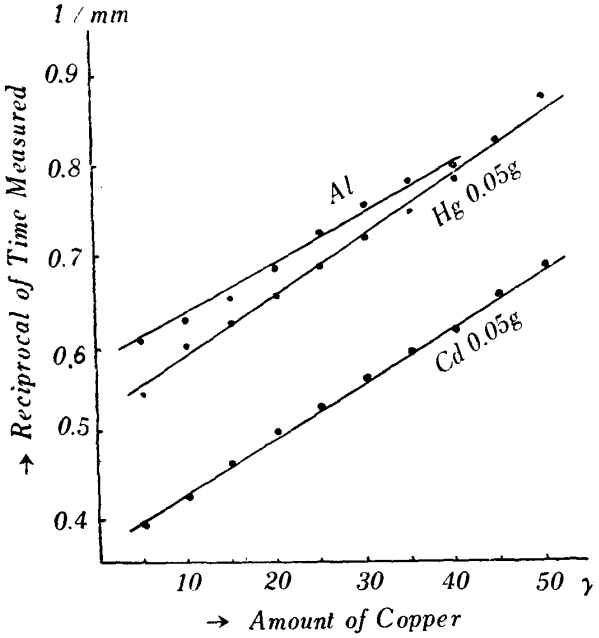

Fig. 4.

Table 5.

Metals	Impurities (%)	Metals taken (g)	Acids used	Time measured (sec)	Cu obtained (%)
Ni	Cu 0.026 Mn 0.003 Co 0.04 Fe 0.17	0.0528 0.0556 0.0481	HNO_3 (1 : 1) 5ml	78 76 79	0.023 0.028 0.027 mean 0.026
Zn	Cu 0.008 Pb 0.009 Si 0.004 As 0.0003	0.4692 0.4906 0.4464	HNO_3 (1 : 1) 6ml	71 69 74	0.0075 0.0077 0.0070 mean 0.0074
	Cu 0.004 Pb 1.05 Cd 0.46 Fd 0.004 S 0.0005	0.5027 0.4911 0.5060	HNO_3 (1 : 1) 6ml	81 84 81	0.0045 0.0040 0.0045 mean 0.0043
Cd	Cu 0.012 Si 0.32 Mn 0.014 Fe 0.52 Mg 0.008	0.0986 0.1014 0.1027	Aqua regia 10ml	94 90 92	0.011 0.016 0.013 mean 0.013
	Cu 0.051 Zn 6.47 Mg 1.84 Mn 0.34	0.0508 0.0486 0.0524	Aqua regia 10ml	84 85 82	0.048 0.048 0.053 mean 0.050

Summary

1) Copper has a catalytic behaviour on the reduction of ferric ion in an acidic solution with thiosulfate. Applying this behaviour, the microdeterminations of copper in various metals were investigated.

2) The suitable concentration of the acids and effects of various metals for the determination were discussed.

3) Under a definite condition, the reciprocals of the time required for the reduction of ferric ion were linear for the amount of copper.

4) Using this linear function, as small amount as 0.001～0.1 per cent of copper in various metals was determined.